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Crystal and molecular structure of the tris(diphenylacetylene)molybdenum(0) monocarbonyl $Mo(CO)(PhC{\equiv}CPh)_3$

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Abstract

The crystal structure of $Mo(CO)(PhC{\equiv}CPh)_3$ formed in the reaction of $Mo(CO)_6$ with diphenylacetylene was determined by the single-crystal X-ray diffraction method. The crystals are orthorhombic, of space group *Pbca*, $a = 19.082(5)$ Å, $b = 22.068(5)$ Å, $c = 31.645(10)$ Å, $V = 1325.8(6)$ Å^3 and $Z = 16$. The structure solved by direct methods has been refined to $R = 0.036$ for 3919 observed reflections. There are two crystallographically independent molecules in the asymmetric unit. The nuclear magnetic resonance as well as the IR and electronic absorption spectroscopies have been used to scrutinize the title compound.

Key words: Molybdenum; Carbonyl; Crystal structure

1. Introduction

The Group 6 metal carbonyls are applied as catalyst precursors in many reactions of acetylenes such as metathesis [1], polymerization [2] or cyclotrimerization [3]. Depending upon conditions, the reaction of metal carbonyls with acetylene groups could give different products in which the acetylenes coordinate to metal as the terminal [4] or bridging ligands and also as the ligands being the products of cyclodimerization or trimerization [5].

In continuation of our research of catalytic activity of the Group 6 metal carbonyls [6], we have investigated the reaction of $Mo(CO)_6$ with acetylenes in the presence of phenol. Our aim was to characterize the compounds formed in the catalytically active system for acetylene metathesis.

One of the products formed in reaction of $Mo(CO)_6$ with diphenylacetylene (studied by the single-crystal X-ray analysis) consists of the binuclear molybdenum units bonded to three terminal carbonyl groups and of one diphenylacetylene, one tetraphenylcyclobutadiene and one tetraphenylcyclobutadienone [4].

The tris(diphenylacetylene)molybdenum monocarbonyl was synthesized many years ago by Strohmeir and Hobe [7] in the reaction of $Mo(CO)_6$ with diphenylacetylene, but its crystal structure has never been determined. We felt it was valid to study the structure of the $Mo(CO)(PhC{\equiv}CPh)_3$ obtained by us as the first example of mononuclear molybdenum(0) carbonyl alkyne complex.

2. Experimental details

2.1. Preparation

$Mo(CO)(PhC{\equiv}CPh)_3$ can be prepared by photochemical or thermal reaction of $Mo(CO)_6$ with $PhC{\equiv}CPh$. The reaction was carried out in heptane solution in the presence of tenfold phenol excess and under a nitrogen atmosphere. $Mo(CO)_6$ (0.5 g, 1.89 mmol), $PhC{\equiv}CPh$ (1.01 g, 5.67 mmol) and phenol (1.78 g, 18.9 mmol) in heptane (100 cm^3) were refluxed or irradiated with a mercury lamp at room temperature for about 2 h. After filtration of the brown precipitate the reaction mixture was evaporated to dryness under reduced pressure. Unreacted $Mo(CO)_6$ and phenol were removed by sublimation. The residue was washed with methanol. Recrystallization from toluene–heptane

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yielded pure yellow crystals which are stable in air (melting point, 145–144°C (decomposition)).

2.2. Spectroscopic studies

The ^1H and ^{13}C NMR spectra were recorded on a Brucker AMX 300 MHz spectrometer in $CDCl_3$ solution.

^1H NMR: δ 7.47, 7.43, 7.28 ppm *ortho*, *meta* and *para* protons of phenyl respectively. ^{13}C NMR: δ 224.3 (CO); 190.0, 170.4 ($C\equiv C$); 140.1; 138.4 ($C_{1\text{-ph}}$); 129.0 ($C_{o\text{-ph}}$); 128.5 ($C_{m\text{-ph}}$); 127.9 ($C_{p\text{-ph}}$) ppm.

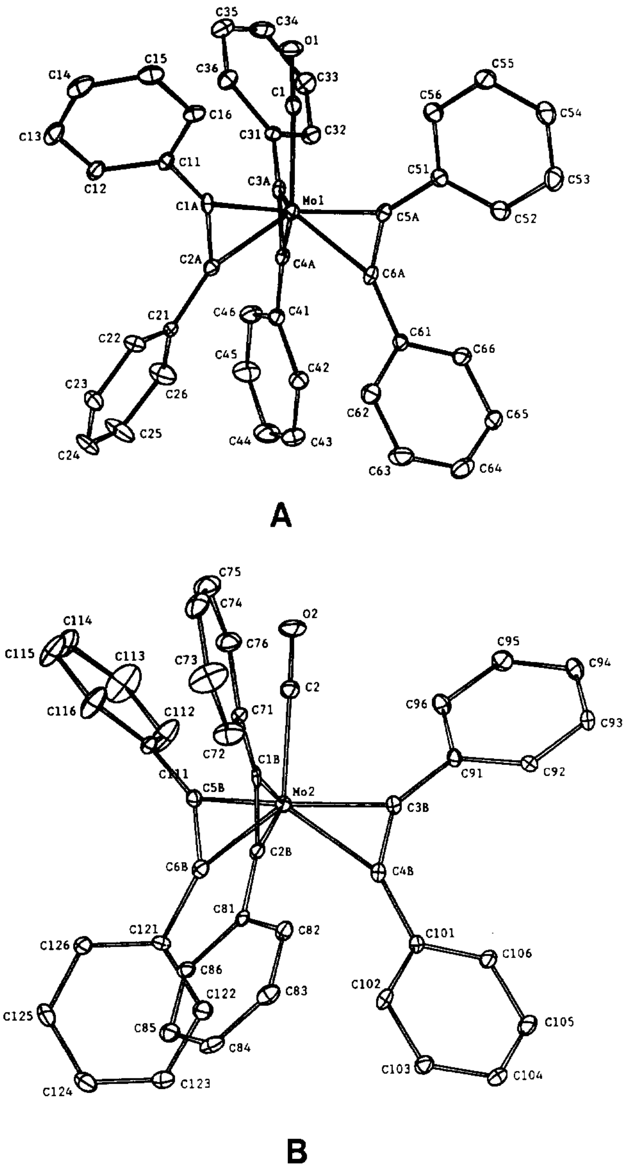

Fig. 1. Perspective view of the $Mo(CO)(PhC\equiv CPh)_3$ showing the atom-numbering scheme for two crystallographically independent molecules A and B, determined in the asymmetric unit. Hydrogen atoms have been omitted for clarity.

TABLE 1. Crystal data and details of refinement

Chemical formula	$C_{43}H_{30}OMo$
Molecular weight	658.7
Space group	*Pbca*
Cell constants	
a (Å)	19.082(5)
b (Å)	22.068(5)
c (Å)	31.645(10)
V (Å^3)	13325.8(6.3)
Z	16
$F(000)$	5408
D_m (Mg m^{-3}) (C_6H_5Cl–$CHCl_3$)	1.32(1)
D_c (Mg m^{-3})	1.313(1)
Radiation	Mo Kα (λ = 0.71069 Å)
μ (cm^{-1})	4.23
Crystal size (mm × mm × mm)	0.6 × 0.6 × 0.3
Reflections determining the lattice	25
2θ range (°)	$22 < 2\theta < 26$
2θ maximum (°)	46
Number of reflections	
Collected	8784
Observed ($I \geq 3.0\sigma(I)$)	3919
Number of variables	811
R	0.036
R_w	0.029
S	1.754
w	$1/\sigma^2(F_o)$
Δ/σ (for non-H atoms)	0.01
$\Delta\rho$	0.32

The IR spectra were obtained on a Specord M80 spectrometer in KBr pellets and heptane solution.

IR (KBr): $\nu(C\equiv O)$ 2060 and 2048 vs, $\nu(C\equiv C)$ 1680wbr cm^{-1} and others in Fig. 3. IR (heptane): $\nu(C\equiv O)$ 2055vs cm^{-1}.

Electronic spectra were measured on a Hewlett-Packard 8452A spectrophotometer in C_6H_6 solution. λ_{max}: 218 (log ϵ = 3.07), 292 (log ϵ = 3.85), 332 (log ϵ = 3.84), 374 (log ϵ = 3.33) nm.

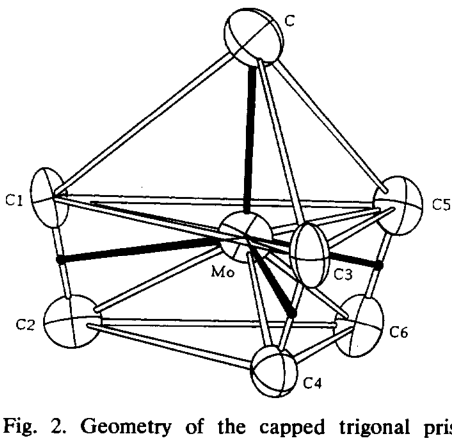

Fig. 2. Geometry of the capped trigonal prismatic coordination polyhedron for the $Mo(CO)(PhC\equiv CPh)_3$ together with the alternative distorted tetrahedron (———).

TABLE 2. Final atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Mo(1)	0.2049(2)	0.2376(2)	0.0075(1)	3.8(2)
Mo(2)	0.0906(2)	0.0003(2)	0.2708(1)	3.3(2)
O(1)	0.2594(2)	0.3742(2)	0.0034(2)	7.4(3)
O(2)	0.0459(2)	−0.1380(2)	0.2729(1)	7.3(3)
C(1)	0.2381(3)	0.3275(2)	0.0046(2)	4.6(3)
C(1A)	0.2646(2)	0.2296(3)	−0.0478(1)	3.7(3)
C(2A)	0.2458(3)	0.1749(2)	−0.0339(2)	3.6(3)
C(3A)	0.2549(2)	0.2390(3)	0.0660(1)	3.7(3)
C(4A)	0.2257(3)	0.1856(2)	0.0606(2)	3.7(3)
C(5A)	0.1036(2)	0.2694(2)	−0.0032(1)	3.6(3)
C(6A)	0.0998(3)	0.2115(2)	0.0047(2)	3.9(3)
C(11)	0.3043(3)	0.2590(2)	−0.0811(1)	3.8(3)
C(12)	0.3648(3)	0.2323(3)	−0.0953(2)	5.3(3)
C(13)	0.4038(3)	0.2567(3)	−0.1272(2)	6.9(4)
C(14)	0.3836(4)	0.3080(3)	−0.1457(2)	7.9(5)
C(15)	0.3233(4)	0.3375(3)	−0.1327(2)	6.6(4)
C(16)	0.2828(3)	0.3122(2)	−0.0994(2)	5.1(3)
C(21)	0.2591(3)	0.1133(2)	−0.0480(2)	3.5(3)
C(22)	0.2697(3)	0.0987(2)	−0.0892(2)	5.3(4)
C(23)	0.2846(3)	0.0413(3)	−0.1031(2)	6.0(4)
C(24)	0.2903(4)	−0.0039(3)	−0.0745(2)	8.4(4)
C(25)	0.2831(5)	0.0093(3)	−0.0336(2)	10.4(5)
C(26)	0.2655(4)	0.0673(3)	−0.0205(2)	8.4(5)
C(31)	0.2950(3)	0.2771(2)	0.0959(1)	3.4(3)
C(32)	0.2766(3)	0.2789(2)	0.1384(2)	5.1(4)
C(33)	0.3141(3)	0.3139(3)	0.1662(2)	6.0(4)
C(34)	0.3699(3)	0.3477(3)	0.1525(2)	6.4(4)
C(35)	0.3891(3)	0.3456(3)	0.1106(2)	6.3(4)
C(36)	0.3523(3)	0.3105(3)	0.0826(2)	5.1(4)
C(41)	0.2221(3)	0.1281(2)	0.0831(2)	3.9(3)
C(42)	0.1730(3)	0.0848(2)	0.0730(2)	4.9(3)
C(43)	0.1697(3)	0.0309(3)	0.0938(2)	6.1(4)
C(44)	0.2136(4)	0.0184(3)	0.1256(2)	7.9(5)
C(45)	0.2614(4)	0.0607(3)	0.1379(2)	7.6(5)
C(46)	0.2657(3)	0.1149(3)	0.1165(2)	5.9(4)
C(51)	0.0541(3)	0.3187(2)	−0.0138(2)	4.2(3)
C(52)	−0.0163(3)	0.3095(3)	−0.0109(2)	5.9(4)
C(53)	−0.0637(3)	0.3555(3)	−0.0204(2)	7.4(5)
C(54)	−0.0391(3)	0.4110(3)	−0.0328(2)	7.0(4)
C(55)	0.0311(3)	0.4203(3)	−0.0365(2)	7.7(5)
C(56)	0.0767(3)	0.3742(3)	−0.0262(2)	6.0(4)
C(61)	0.0478(3)	0.1645(2)	0.0067(2)	3.7(3)
C(62)	0.0456(3)	0.1185(3)	−0.0224(2)	5.9(4)
C(63)	−0.0065(4)	0.0759(3)	−0.0224(2)	7.4(5)
C(64)	−0.0575(3)	0.0794(3)	0.0063(2)	7.0(4)
C(65)	−0.0561(3)	0.1220(3)	0.0379(2)	6.4(4)
C(66)	−0.0035(3)	0.1654(3)	0.0368(2)	5.4(4)
C(2)	0.0619(3)	−0.0899(2)	0.2717(2)	4.3(3)
C(1B)	0.0359(2)	0.0132(2)	0.2147(1)	3.3(3)
C(2B)	0.0639(2)	0.0651(2)	0.2256(2)	3.1(3)
C(3B)	0.1915(2)	−0.0366(2)	0.2737(1)	3.0(2)
C(4B)	0.1964(2)	0.0220(2)	0.2694(1)	3.1(3)
C(5B)	0.0323(2)	−0.0004(2)	0.3263(1)	3.3(3)
C(6B)	0.0578(3)	0.0536(2)	0.3213(2)	3.3(3)
C(71)	−0.0105(3)	−0.0135(2)	0.1827(2)	3.5(3)
C(72)	−0.0282(4)	0.0198(3)	0.1477(2)	7.5(5)
C(73)	−0.0753(4)	−0.0033(4)	0.1188(2)	10.8(6)
C(74)	−0.1053(3)	−0.0572(3)	0.1237(2)	7.8(5)
C(75)	−0.0887(4)	−0.0901(3)	0.1578(2)	7.3(4)
C(76)	−0.0412(3)	−0.0679(3)	0.1868(2)	6.1(4)
C(81)	0.0655(2)	0.1273(2)	0.2107(2)	2.9(3)
C(82)	0.0900(3)	0.1419(2)	0.1702(2)	4.1(3)
C(83)	0.0899(3)	0.2018(2)	0.1567(2)	4.8(3)
C(84)	0.0653(3)	0.2464(3)	0.1817(2)	5.2(3)
C(85)	0.0405(3)	0.2327(2)	0.2213(2)	4.6(3)
C(86)	0.0416(2)	0.1733(2)	0.2359(2)	3.4(3)
C(91)	0.2313(2)	−0.0923(2)	0.2731(2)	3.1(3)
C(92)	0.2884(3)	−0.0996(2)	0.2464(2)	3.8(3)
C(93)	0.3267(3)	−0.1516(2)	0.2465(2)	4.6(3)
C(94)	0.3098(3)	−0.1983(2)	0.2723(2)	6.0(4)
C(95)	0.2539(3)	−0.1931(2)	0.2983(2)	5.2(3)
C(96)	0.2140(3)	−0.1406(2)	0.2991(2)	4.4(3)
C(101)	0.2503(2)	0.0668(2)	0.2624(1)	2.8(3)
C(102)	0.2327(3)	0.1253(2)	0.2490(2)	3.8(3)
C(103)	0.2839(3)	0.1674(2)	0.2377(2)	4.3(3)
C(104)	0.3536(3)	0.1517(2)	0.2404(2)	5.0(3)
C(105)	0.3706(3)	0.0960(2)	0.2561(2)	5.6(4)
C(106)	0.3202(3)	0.0534(2)	0.2665(2)	4.6(3)
C(111)	−0.0125(3)	−0.0394(2)	0.3538(2)	3.3(3)
C(112)	0.0119(3)	−0.0666(4)	0.3880(2)	8.8(5)
C(113)	−0.0312(4)	−0.1038(4)	0.4113(2)	12.2(7)
C(114)	−0.0985(4)	−0.1122(3)	0.4027(2)	7.8(5)
C(115)	−0.1221(3)	−0.0862(4)	0.3682(2)	9.1(5)
C(116)	−0.0788(3)	−0.0495(3)	0.3447(2)	8.5(5)
C(121)	0.0534(3)	0.1138(2)	0.3400(2)	3.2(3)
C(122)	0.1111(3)	0.1506(2)	0.3423(2)	4.5(3)
C(123)	0.1048(3)	0.2078(2)	0.3597(2)	5.4(4)
C(124)	0.0413(3)	0.2290(3)	0.3732(2)	6.3(4)
C(125)	−0.0156(3)	0.1923(3)	0.3703(2)	6.4(4)
C(126)	−0.0105(3)	0.1350(2)	0.3539(2)	4.6(3)

$B_{eq} = \frac{1}{3}\Sigma_{ij} B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

2.3. X-ray analysis

The yellow crystals of dimensions 0.6 mm × 0.6 mm × 0.3 mm were used for the data collection. The density was measured by flotation. The space groups and approximate unit-cell dimensions were determined from rotation and Weissenberg photographs. The diffraction data were measured on a KM4 κ-axis computer-controlled four-circle diffractometer with graphite-monochromated Mo Kα radiation. The diffracted intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction. The details of the crystal data intensity measurements are given in Table 1.

The structure was solved by direct methods with the SHELXS-86 program [8] and refined by the full-matrix least-squares method, using the SYNTEX XTL/XTLE structure determination system [9], locally adopted by Mr. A. Kowalski for calculation on the IBM PC/AT computer. All non-hydrogen atoms were refined with anisotropic thermal parameters. A difference Fourier map clearly afforded the positions of the hydrogen atoms and their positional parameters were incorporated into subsequent refinement cycles. Refinement

TABLE 3. H-atom coordinates and isotropic thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	B_{iso} (Å^2)
H(12)	0.381(0)	0.194(0)	−0.082(0)	7.5(0)
H(13)	0.448(0)	0.236(0)	−0.137(0)	7.5(0)
H(14)	0.412(0)	0.325(0)	−0.169(0)	7.5(0)
H(15)	0.309(0)	0.376(0)	−0.146(0)	7.5(0)
H(16)	0.239(0)	0.332(0)	−0.090(0)	7.5(0)
H(22)	0.265(0)	0.132(0)	−0.110(0)	7.5(0)
H(23)	0.292(0)	0.033(0)	−0.134(0)	7.5(0)
H(24)	0.300(0)	−0.046(0)	−0.084(0)	7.5(0)
H(25)	0.290(0)	−0.023(0)	−0.012(0)	7.5(0)
H(26)	0.257(0)	0.074(0)	0.010(0)	7.5(0)
H(32)	0.236(0)	0.255(0)	0.149(0)	7.5(0)
H(33)	0.301(0)	0.314(0)	0.197(0)	7.5(0)
H(34)	0.396(0)	0.374(0)	0.173(0)	7.5(0)
H(35)	0.431(0)	0.369(0)	0.100(0)	7.5(0)
H(36)	0.366(0)	0.309(0)	0.052(0)	7.5(0)
H(42)	0.139(0)	0.093(0)	0.050(0)	7.5(0)
H(43)	0.135(0)	−0.000(0)	0.085(0)	7.5(0)
H(44)	0.210(0)	−0.021(0)	0.141(0)	7.5(0)
H(45)	0.294(0)	0.052(0)	0.162(0)	7.5(0)
H(46)	0.301(0)	0.146(0)	0.125(0)	7.5(0)
H(52)	−0.034(0)	0.269(0)	−0.001(0)	7.5(0)
H(53)	−0.115(0)	0.348(0)	−0.018(0)	7.5(0)
H(54)	−0.072(0)	0.444(0)	−0.039(0)	7.5(0)
H(55)	0.049(0)	0.460(0)	−0.046(0)	7.5(0)
H(56)	0.128(0)	0.382(0)	−0.028(0)	7.5(0)
H(62)	0.084(0)	0.116(0)	−0.044(0)	7.5(0)
H(63)	−0.006(0)	0.043(0)	−0.044(0)	7.5(0)
H(64)	−0.097(0)	0.050(0)	0.004(0)	7.5(0)
H(65)	−0.092(0)	0.122(0)	0.061(0)	7.5(0)
H(66)	−0.003(0)	0.198(0)	0.058(0)	7.5(0)
H(72)	−0.008(0)	0.061(0)	0.144(0)	7.5(0)
H(73)	−0.085(0)	0.021(0)	0.093(0)	7.5(0)
H(74)	−0.140(0)	−0.072(0)	0.103(0)	7.5(0)
H(75)	−0.111(0)	−0.131(0)	0.162(0)	7.5(0)
H(76)	−0.029(0)	−0.094(0)	0.212(0)	7.5(0)
H(82)	0.107(0)	0.109(0)	0.151(0)	7.5(0)
H(83)	0.108(0)	0.212(0)	0.128(0)	7.5(0)
H(84)	0.066(0)	0.289(0)	0.172(0)	7.5(0)
H(85)	0.021(0)	0.265(0)	0.240(0)	7.5(0)
H(86)	0.025(0)	0.164(0)	0.265(0)	7.5(0)
H(92)	0.302(0)	−0.066(0)	0.227(0)	7.5(0)
H(93)	0.368(0)	−0.155(0)	0.227(0)	7.5(0)
H(94)	0.338(0)	−0.236(0)	0.272(0)	7.5(0)
H(95)	0.241(0)	−0.228(0)	0.317(0)	7.5(0)
H(96)	0.173(0)	−0.137(0)	0.319(0)	7.5(0)
H(102)	0.182(0)	0.137(0)	0.248(0)	7.5(0)
H(103)	0.270(0)	0.209(0)	0.228(0)	7.5(0)
H(104)	0.391(0)	0.180(0)	0.231(0)	7.5(0)
H(105)	0.421(0)	0.085(0)	0.260(0)	7.5(0)
H(106)	0.335(0)	0.012(0)	0.277(0)	7.5(0)
H(112)	0.062(0)	−0.060(0)	0.397(0)	7.5(0)
H(113)	−0.010(0)	−0.125(0)	0.436(0)	7.5(0)
H(114)	−0.129(0)	−0.137(0)	0.421(0)	7.5(0)
H(115)	−0.172(0)	−0.092(0)	0.359(0)	7.5(0)
H(116)	−0.099(0)	−0.029(0)	0.319(0)	7.5(0)
H(122)	0.157(0)	0.136(0)	0.331(0)	7.5(0)
H(123)	0.147(0)	0.234(0)	0.362(0)	7.5(0)
H(124)	0.037(0)	0.271(0)	0.385(0)	7.5(0)
H(125)	−0.062(0)	0.207(0)	0.380(0)	7.5(0)
H(126)	−0.053(0)	0.108(0)	0.352(0)	7.5(0)

TABLE 4. Anisotropic thermal parameters with estimated standard deviations in parentheses [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	3.58(2)	3.78(2)	3.98(2)	0.09(2)	0.55(2)	0.19(2)
Mo(2)	2.82(2)	2.92(2)	4.04(2)	0.05(2)	0.28(2)	0.22(2)
O(1)	6.93(3)	3.68(2)	11.58(3)	−1.15(2)	−1.57(3)	1.85(2)
O(2)	7.89(3)	3.23(2)	10.87(3)	−1.63(2)	0.07(3)	0.99(2)
C(1)	4.11(3)	4.73(3)	5.08(3)	0.83(3)	0.54(3)	0.36(3)
C(1A)	2.48(3)	5.67(3)	3.06(3)	1.59(2)	−0.29(2)	0.15(2)
C(2A)	3.12(3)	3.78(3)	3.77(3)	−0.12(2)	−0.31(3)	0.54(2)
C(3A)	2.72(2)	4.79(3)	3.69(3)	0.81(3)	0.94(2)	0.86(3)
C(4A)	3.03(3)	4.11(3)	4.04(3)	−0.28(2)	1.16(2)	−0.11(2)
C(5A)	3.62(3)	5.02(3)	2.27(2)	−0.31(2)	0.92(2)	0.58(2)
C(6A)	2.72(3)	5.82(3)	3.19(3)	−0.39(2)	0.37(3)	0.07(2)
C(11)	3.24(3)	4.91(3)	3.12(2)	−0.61(3)	0.72(2)	0.06(2)
C(12)	3.87(3)	6.44(4)	5.66(4)	−1.38(3)	0.61(3)	−1.04(3)
C(13)	5.75(3)	9.54(5)	5.33(3)	−2.15(4)	2.30(3)	−0.57(4)
C(14)	9.03(5)	9.57(5)	5.05(4)	−4.21(4)	2.12(4)	1.15(4)
C(15)	8.29(5)	5.92(4)	5.73(4)	−1.61(4)	−1.15(3)	1.23(3)
C(16)	6.69(4)	4.56(3)	3.94(3)	−1.56(3)	0.50(3)	1.84(2)
C(21)	3.00(3)	3.18(3)	4.31(3)	−0.34(2)	0.84(2)	0.30(2)
C(22)	6.88(4)	3.39(3)	5.56(4)	0.04(3)	−0.38(3)	−0.03(3)
C(23)	6.25(4)	4.96(4)	6.73(4)	0.97(3)	0.47(4)	−1.31(3)
C(24)	10.18(5)	3.58(3)	11.42(5)	2.04(5)	1.53(4)	−2.57(4)
C(25)	19.52(8)	3.89(4)	7.85(4)	3.21(5)	4.00(5)	0.37(3)
C(26)	14.39(7)	5.59(4)	5.38(4)	0.01(4)	3.60(4)	−0.31(3)
C(31)	3.61(3)	2.90(3)	3.82(3)	0.14(2)	0.08(3)	0.75(2)
C(32)	5.11(4)	5.28(4)	4.98(3)	−0.81(3)	0.10(3)	−0.16(3)
C(33)	6.62(4)	7.08(4)	4.29(3)	−0.84(4)	0.14(3)	−0.89(3)
C(34)	7.03(4)	4.50(4)	7.74(5)	−1.45(3)	−2.60(4)	−0.66(3)
C(35)	5.60(4)	6.11(4)	7.28(4)	−1.94(3)	−0.11(3)	0.99(3)
C(36)	4.37(3)	6.13(4)	4.84(3)	−0.64(3)	−0.49(3)	0.84(3)
C(41)	3.76(3)	3.86(3)	4.01(3)	0.17(3)	0.08(2)	0.34(2)
C(42)	5.79(4)	4.62(3)	4.40(3)	−0.09(3)	0.37(3)	0.92(3)
C(43)	7.16(4)	5.27(4)	5.79(4)	−1.55(3)	−0.50(3)	1.18(3)
C(44)	9.34(5)	4.35(4)	9.89(5)	−0.21(4)	−0.83(5)	3.02(3)
C(45)	8.92(5)	5.51(4)	8.36(5)	0.09(4)	−3.24(4)	2.97(3)
C(46)	5.18(4)	4.48(3)	8.19(4)	−0.57(3)	−2.09(3)	1.62(3)
C(51)	4.60(3)	4.42(3)	3.74(3)	0.31(3)	0.08(3)	−0.20(3)
C(52)	4.50(3)	5.14(4)	8.23(5)	0.86(3)	−1.89(3)	0.18(3)
C(53)	5.06(4)	8.34(5)	8.69(5)	1.45(4)	−0.52(4)	0.60(4)
C(54)	6.17(4)	6.47(4)	8.44(5)	1.99(4)	−0.77(4)	0.58(4)
C(55)	5.99(4)	4.78(4)	12.41(6)	0.78(4)	0.46(4)	2.95(4)
C(56)	5.04(4)	4.73(3)	8.32(4)	0.97(3)	−0.64(3)	1.21(3)
C(61)	3.30(3)	3.71(3)	4.02(3)	0.41(2)	−0.02(3)	0.28(2)
C(62)	6.31(4)	6.10(4)	5.19(4)	−0.35(3)	0.93(3)	0.50(3)
C(63)	8.78(5)	5.58(4)	7.77(5)	−2.19(4)	−0.24(4)	−1.51(3)
C(64)	4.71(3)	6.70(4)	9.67(5)	−1.41(3)	−1.51(4)	2.17(4)
C(65)	5.46(4)	5.37(4)	8.30(5)	0.00(3)	3.18(4)	1.23(3)
C(66)	5.46(4)	4.91(4)	5.73(4)	−0.82(3)	1.62(3)	−0.64(3)
C(2)	3.86(3)	3.53(3)	5.38(3)	−0.08(2)	−0.15(3)	0.42(3)
C(1B)	1.84(2)	4.83(3)	3.38(3)	1.82(2)	0.57(2)	−0.07(2)
C(2B)	2.06(2)	3.39(3)	3.90(3)	−0.22(2)	0.05(2)	0.35(2)
C(3B)	3.12(3)	3.28(3)	2.62(2)	0.58(2)	0.14(2)	0.42(2)
C(4B)	2.65(2)	3.90(3)	2.89(2)	0.43(2)	0.18(3)	0.15(2)
C(5B)	2.84(2)	3.26(2)	3.75(3)	0.46(3)	−0.10(2)	−0.19(3)
C(6B)	2.58(3)	3.42(3)	3.92(3)	0.28(2)	−0.57(2)	0.99(2)
C(71)	2.56(3)	3.50(4)	4.41(3)	−0.41(2)	0.25(2)	−0.85(2)
C(72)	8.60(5)	6.81(5)	7.20(4)	−1.49(4)	−3.60(4)	0.95(3)
C(73)	12.34(6)	13.91(6)	6.24(4)	−4.37(6)	−5.15(4)	2.66(5)
C(74)	4.42(4)	11.63(6)	7.32(4)	−2.31(4)	−0.67(3)	−4.06(4)
C(75)	7.02(4)	7.94(4)	7.07(4)	−2.49(4)	−0.52(4)	−1.66(4)
C(76)	5.92(4)	5.52(4)	6.87(4)	−1.04(3)	−1.78(3)	−1.04(3)

TABLE 4. (continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(81)	1.42(2)	3.15(3)	4.07(3)	0.00(2)	−0.68(2)	0.13(2)
C(82)	3.17(3)	4.56(3)	4.65(3)	−0.19(3)	0.40(3)	0.80(3)
C(83)	4.61(3)	4.96(3)	4.83(3)	−1.27(3)	−0.83(3)	1.89(3)
C(84)	4.27(3)	4.30(3)	6.98(4)	−1.67(3)	−2.31(3)	1.63(3)
C(85)	3.45(3)	4.17(3)	6.17(4)	0.01(3)	−1.52(3)	−0.29(3)
C(86)	2.61(3)	3.24(3)	4.37(4)	−0.23(2)	−1.03(3)	0.26(2)
C(91)	2.52(2)	3.13(3)	3.54(3)	0.88(2)	−0.13(2)	0.42(2)
C(92)	3.65(3)	3.00(3)	4.89(3)	0.08(3)	0.40(3)	−0.65(2)
C(93)	2.98(3)	4.35(3)	6.42(4)	0.65(3)	1.06(3)	−1.00(3)
C(94)	4.38(3)	3.88(3)	9.63(5)	1.84(3)	0.37(4)	0.44(3)
C(95)	4.90(3)	3.51(3)	7.14(4)	0.46(3)	−0.32(3)	1.69(3)
C(96)	4.69(3)	3.96(3)	4.69(3)	1.15(3)	0.15(3)	0.38(2)
C(101)	2.90(3)	3.36(3)	2.13(3)	0.37(2)	0.37(2)	0.66(2)
C(102)	2.30(3)	5.25(3)	3.94(3)	−0.47(3)	−0.21(2)	0.87(3)
C(103)	3.52(3)	3.56(3)	5.80(3)	−0.26(3)	−0.53(3)	0.89(3)
C(104)	3.80(3)	4.20(3)	7.03(4)	−1.29(3)	1.04(3)	0.25(3)
C(105)	2.47(3)	5.02(3)	9.37(5)	−0.08(3)	−1.23(3)	0.06(3)
C(106)	2.74(3)	3.43(3)	7.59(4)	−0.01(2)	0.06(3)	0.36(3)
C(111)	2.81(3)	3.61(3)	3.48(3)	−0.57(2)	0.50(2)	0.66(2)
C(112)	5.83(4)	14.14(7)	6.46(4)	−3.54(4)	−0.29(4)	6.49(4)
C(113)	11.21(7)	17.69(8)	7.60(5)	−2.43(6)	−0.65(5)	9.11(5)
C(114)	6.49(4)	8.94(5)	8.00(5)	−2.08(4)	2.62(4)	3.42(4)
C(115)	4.05(4)	12.05(6)	11.29(6)	−2.31(4)	0.36(4)	5.14(5)
C(116)	4.59(4)	12.04(6)	9.00(5)	−1.90(4)	−0.38(4)	6.45(4)
C(121)	4.07(3)	2.36(3)	3.05(3)	−0.24(2)	−0.06(2)	−0.36(2)
C(122)	4.80(4)	4.24(3)	4.33(3)	−0.48(3)	0.82(2)	−0.25(3)
C(123)	5.25(4)	4.74(3)	6.36(4)	−1.42(3)	−0.21(3)	−1.42(3)
C(124)	7.68(5)	3.87(3)	7.37(4)	0.24(3)	1.17(4)	−1.55(3)
C(125)	6.04(4)	5.14(4)	8.09(5)	1.04(3)	2.83(4)	−1.77(3)
C(126)	4.46(3)	4.05(3)	5.35(4)	−0.93(3)	1.56(3)	−0.81(3)

[a] The temperature factor is of the form $T = \exp[-\frac{1}{4}(B_{11}h_a^{2*2} + B_{22}k_b^{2*2} + B_{33}l_c^{2*2} + 2B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c)]$.

to convergence led to $R = 0.036$ and $R_w = 0.029$. Neutral atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [10].

3. Discussion

A view of the $Mo(CO)(PhC\equiv CPh)_3$ showing the atom-numbering scheme, for two crystallographically independent molecules A and B determined in the asymmetric unit is given in Fig. 1. Final atomic parameters are collected in Table 2 and the H-atom coordinates are given in Table 3. In Table 4 are gathered the anisotropic thermal parameters. Selected interatomic distances and angles are listed in Tables 5 and 6. The geometry of the molecule, shown in Fig. 2, is essentially of C_{3v} symmetry (exclusive of the phenyl groups which are of course free to rotate). The coordination around the molybdenum atom may be described as the capped trigonal prism with the capping position in the base and three bidentate alkyne ligands. The presence of a CO group as the capping ligand in the taper of trigonal prism leads to the repulsion of the nearest three acetylene carbon atoms away from the carbonyl group. These acetylene carbon atoms C(1), C(3) and C(5) form an almost equilateral triangle of an average length 3.596(7) Å while C(2), C(4) and C(6) define a considerably smaller triangle of an average dimension 3.080(7) Å (Fig. 2). The acetylene carbon atoms define two parallel planes. The angles between the normal to the plane are 0.25° and 0.60° for Mo(1) and Mo(2) molecules respectively. Molybdenum is lifted from its central position between two parallel planes towards the CO group (Table 7). The phenyl-carbon-defining planes are bent and twisted from the acetylene carbon plane to various degrees.

The geometry of the coordinated diphenylacetylene molecules is normal for an acetylene complex [11]: the C(ac)–C(ac) bond length increased to 1.321(8) Å relative to the value of 1.21 Å for that in diphenylacetylene itself [12] and the bond angles at the acetylene carbon atoms are decreased to 150.8(8) (Mo(1)) and 147.0(5)° (Mo(2)) so that the diphenylacetylene molecules acquire a *cis*-stilbene configuration.

The average C_{ph}–C_{ph} distance in the phenyl rings is 1.367(8) Å with an average C_{ph}–C_{ph}–C_{ph} angle of 120.0(6)°. The Mo(1)–C(1) and C(1)–O(1) distances associated with the carbonyl group are 2.086(5) Å and 1.107(7) Å respectively but the Mo(2)–C(2) and C(2)–O(2) distances are 2.066(5) and 1.104(6) Å respectively. These small differences in the atomic distances lead to the splitting band assigned to the C≡O stretching vibration observed in the IR spectra of the investigated

TABLE 5. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Bond distances			
Mo(1)–C(1)	2.086(5)	Mo(2)–C(3B)	2.093(5)
Mo(2)–C(2)	2.066(5)	Mo(2)–C(5B)	2.079(5)
C(1)–O(1)	1.107(7)	Mo(2)–C(2B)	2.085(5)
C(2)–O(2)	1.104(6)	Mo(2)–C(4B)	2.075(5)
Mo(1)–C(1A)	2.097(5)	Mo(2)–C(6B)	2.083(5)
Mo(1)–C(3A)	2.084(5)	C(1A)–C(2A)	1.333(8)
Mo(1)–C(5A)	2.085(5)	C(3A)–C(4A)	1.317(8)
Mo(1)–C(2A)	2.060(5)	C(5A)–C(6A)	1.304(7)
Mo(1)–C(4A)	2.071(5)	C(1B)–C(2B)	1.315(7)
M(1)–C(6A)	2.089(5)	C(3B)–C(4B)	1.306(7)
Mo(2)–C(1B)	2.080(5)	C(5B)–C(6B)	1.297(7)
Bond angles			
C(1)–Mo(1)–(1A)	82.9(2)	C(3A)–Mo(1)–C(4A)	37.0(2)
C(1)–Mo(1)–C(3A)	83.5(2)	C(5A)–Mo(1)–C(6A)	36.4(2)
C(1)–Mo(1)–C(5A)	87.4(2)	C(1B)–Mo(2)–C(2B)	36.7(2)
C(1)–Mo(2)–C(1B)	90.6(2)	C(3B)–Mo(2)–C(4B)	36.5(2)
C(1)–Mo(2)–C(3B)	82.4(2)	C(5A)–Mo(2)–C(6A)	36.3(2)
C(1)–Mo(2)–C(5B)	80.7(2)	C(1A)–Mo(1)–C(3A)	119.6(2)
O(1)–C(1)–Mo(1)	176.2(5)	C(1A)–Mo(1)–C(5A)	113.3(2)
O(2)–C(2)–Mo(2)	178.6(5)	C(1B)–Mo(2)–C(3B)	123.6(2)
C(1A)–Mo(1)–C(2A)	37.4(2)	C(1B)–Mo(2)–C(5B)	116.9(2)

TABLE 6. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

	n = 1	*n* = 2	*n* = 3	*n* = 4	*n* = 5	*n* = 6
Bond lengths						
Mo(1)–C(*n*)	2.086(5)					
Mo(2)–C(*n*)		2.066(5)				
C(*n*)–O(*n*)	1.107(7)	1.104(6)				
Mo(1)–C(*n*A)	2.097(5)	2.060(5)	2.084(5)	2.071(5)	2.085(5)	2.089(5)
Mo(2)–C(*n*B)	2.080(5)	2.085(5)	2.093(5)	2.075(5)	2.079(5)	2.083(5)
C(1A)–C(*n*A)		1.333(8)				
C(3A)–C(*n*A)				1.317(8)		
C(5A)–C(*n*A)						1.304(7)
C(1B)–C(*n*B)		1.315(7)				
C(3B)–C(*n*B)				1.306(7)		
C(5B)–C(*n*B)						1.297(7)
C(*n*A)–C(*n*1)	1.449(7)	1.455(7)	1.478(7)	1.456(7)	1.478(7)	1.436(7)
C(*n*B)–C((*n* + 6)1)	1.466(7)	1.451(7)	1.444(7)	1.444(7)	1.493(7)	1.456(7)
C(1*n*)–C(1(*n* + 1))	1.373(8)	1.363(8)	1.333(10)	1.386(10)	1.419(9)	1.374(8)
C(2*n*)–C(2(*n* + 1))	1.357(8)	1.371(8)	1.350(9)	1.334(9)	1.387(9)	1.343(8)
C(3*n*)–C(3(*n* + 1))	1.392(7)	1.371(8)	1.369(9)	1.379(9)	1.372(9)	1.382(8)
C(4*n*)–C(4(*n* + 1))	1.378(8)	1.360(8)	1.340(10)	1.363(10)	1.377(9)	1.378(8)
C(5*n*)–C(5(*n* + 1))	1.362(8)	1.393(9)	1.368(10)	1.359(9)	1.379(9)	1.357(8)
C(6*n*)–C(6(*n* + 1))	1.373(8)	1.369(9)	1.331(10)	1.374(9)	1.388(9)	1.366(8)
C(7*n*)–C(7(*n* + 1))	1.371(8)	1.379(10)	1.330(11)	1.339(10)	1.379(9)	1.342(8)
C(8*n*)–C(8(*n* + 1))	1.404(7)	1.389(8)	1.346(8)	1.374(8)	1.390(7)	1.369(7)
C(9*n*)–C(9(*n* + 1))	1.389(7)	1.361(7)	1.354(8)	1.351(9)	1.386(8)	1.385(7)
C(10*n*)–C(10(*n* + 1))	1.399(7)	1.386(7)	1.377(7)	1.364(8)	1.384(8)	1.373(7)
C(11*n*)–C(11(*n* + 1))	1.322(9)	1.376(11)	1.324(11)	1.314(10)	1.376(10)	1.315(8)
C(12*n*)–C(12(*n* + 1))	1.331(8)	1.382(8)	1.367(9)	1.358(9)	1.371(8)	1.378(8)
Bond angles						
C(1)–Mo(1)–C(*n*A)	82.9(2)	119.6(2)	83.5(2)	120.4(2)	87.4(2)	123.5(2)
C(2)–Mo(2)–C(*n*B)	90.6(2)	127.3(2)	82.4(2)	118.8(2)	80.7(2)	117.0(2)
C(1A)–Mo(1)–C(*n*A)		37.4(2)	119.6(2)	121.7(2)	113.3(2)	117.6(2)
C(2A)–Mo(1)–C(*n*A)			113.7(2)	94.1(2)	118.3(2)	98.8(2)
C(3A)–Mo(1)–C(*n*A)				37.0(2)	124.4(2)	118.9(2)
C(4A)–Mo(1)–C(*n*A)					119.8(2)	122.7(2)
C(5A)–Mo(1)–C(*n*A)						36.4(2)
C(1B)–Mo(2)–C(*n*B)		36.7(2)	123.6(2)	116.1(2)	116.9(2)	115.3(2)
C(2B)–Mo(2)–C(*n*B)			121.5(2)	93.7(2)	116.9(2)	93.7(2)
C(3B)–Mo(2)–C(*n*B)				36.5(2)	116.9(2)	117.6(2)
C(4B)–Mo(2)–C(*n*B)					122.7(2)	100.3(2)
C(5B)–Mo(2)–C(*n*B)						36.3(2)
O(*n*)–C(*n*)–Mo(*n*)	176.2(5)	178.6(5)				
Mo(1)–C(*n*A)–C((*n* + 1)A)	69.8(3)		71.0(3)		72.0(3)	
Mo(1)–C(*n*A)–C((*n* − 1)A)		72.8(3)		72.0(3)		71.6(3)
Mo(2)–C(*n*B)–C((*n* + 1)B)	71.8(3)		71.0(3)		72.0(3)	
Mo(2)–C(*n*B)–C((*n* − 1)B)		71.4(3)		72.5(3)		71.7(3)
Mo(1)–C(*n*A)–C((*n*1))	148.5(4)	152.8(4)	144.5(4)	158.5(4)	151.2(4)	149.4(4)
Mo(2)–C(*n*B)–C((*n* + 6)1)	146.8(4)	150.0(4)	144.5(4)	148.7(4)	143.5(4)	147.6(4)
C(*n*1)–C(*n*A)–C((*n* + 1)A)	141.7(5)		144.4(5)		136.8(5)	
C(*n*1)–C(*n*A)–C((*n* − 1)A)		134.3(5)		137.3(5)		139.0(5)
C((*n* + 6)1)–C(*n*B)–C((*n* + 1)B)	141.2(5)		143.6(5)		144.5(5)	
C((*n* + 6)1)–C(*n*B)–C((*n* − 1)B)		138.5(5)		138.3(5)		140.2(5)
C(*n*2)–C(*n*1)–C(*n*A)	119.1(5)	122.8(5)	120.2(5)	121.5(5)	120.3(5)	121.7(5)
C(*n*6)–C(*n*1)–C(*n*A)	122.3(5)	121.6(5)	121.1(5)	122.2(5)	121.8(5)	121.1(5)
C(*n*2)–C(*n*1)–C(*n*6)	118.7(5)	115.5(5)	118.7(5)	116.3(5)	117.9(5)	117.2(5)
C(*n*3)–C(*n*2)–C(*n*1)	122.2(6)	123.9(6)	120.2(5)	121.8(5)	121.2(6)	122.0(6)
C(*n*4)–C(*n*3)–C(*n*2)	120.3(6)	119.0(6)	120.7(6)	121.0(6)	119.4(6)	119.5(6)
C(*n*5)–C(*n*4)–C(*n*3)	120.5(6)	118.8(7)	119.5(6)	119.6(6)	119.9(6)	121.5(6)
C(*n*6)–C(*n*5)–C(*n*4)	119.3(6)	121.1(7)	120.3(6)	119.7(6)	119.3(6)	117.9(6)
C(*n*1)–C(*n*6)–C(*n*5)	119.2(5)	121.7(7)	120.6(5)	121.7(6)	122.3(6)	121.7(6)
C((*n* + 6)2)–C((*n* + 6)1)–C(*n*B)	119.4(5)	121.4(5)	121.2(4)	120.4(4)	122.5(5)	121.1(5)
C((*n* + 6)6)–C((*n* + 6)1)–C(*n*B)	123.8(5)	120.4(4)	121.5(5)	122.0(4)	121.4(5)	119.3(5)
C((*n* + 6)2)–C((*n* + 6)1)–C((*n* + 6)6)	116.7(5)	118.2(5)	117.3(5)	117.5(5)	116.1(6)	119.6(5)

TABLE 6. (continued)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
C((n + 6)3)–C((n + 6)2)–C((n + 6)1)	119.9(6)	119.9(5)	121.2(5)	121.5(5)	119.9(7)	119.4(5)
C((n + 6)4)–C((n + 6)3)–C((n + 6)2)	122.2(7)	121.1(5)	121.0(5)	119.5(5)	123.6(8)	121.1(6)
C((n + 6)5)–C((n + 6)4)–C((n + 6)3)	118.5(4)	119.7(5)	119.3(6)	118.7(5)	116.2(7)	118.8(6)
C((n + 6)6)–C((n + 6)5)–C((n + 6)4)	120.0(6)	120.4(5)	121.1(5)	122.3(5)	120.0(7)	121.3(6)
C((n + 6)1)–C((n + 6)6)–C((n + 6)5)	122.7(6)	120.8(5)	120.1(5)	120.3(5)	124.1(7)	119.7(5)

compound in crystalline form. In solution, $Mo(CO)(PhC{\equiv}CPh)_3$ exhibits only one strong IR absorption band attributed to the carbon monoxide ligand. Weak and rather broad absorption at 1680 cm^{-1} is due to the $C{\equiv}C$ stretching vibration of the coordinated acetylene groups (Fig. 3).

TABLE 7. Coefficients in equations of the type $AX + BY + CZ + D = 0$ for the least-squares planes and deviations of atoms from these planes (Å) with estimated standard deviations in parentheses [a]

Plane	Atoms defining plane	Other atom	Deviation (Å)	A	B	C	D
I	C(1A) C(3A) C(5A)	Mo(1)	−0.197(1)	0.257	0.966	−0.043	6.252
II	C(2A) C(4A) C(6A)	Mo(1)	1.074(1)	0.261	0.965	0.042	4.992
III	C(1B) C(3B) C(5B)	Mo(2)	−0.194(5)	−0.297	−0.951	−0.087	−1.068
IV	C(2B) C(4B) C(6B)	Mo(2)	1.069(5)	−0.306	−0.948	−0.091	−2.386

[a] The angles between the normals to the planes are as follows: plane I–plane II, 0.25°; plane III–plane IV, 0.60°.

In ^{13}C NMR spectra of $Mo(CO)(PhC{\equiv}CPh)_3$ a double acetylene carbon resonance is observed at 190.0 and 170.4 ppm downfield from Me_4Si. It is consistent with a structure which establishes the existence of asymmetric acetylene molybdenum bond about the midpoint of the alkyne. This result suggests that a seven-coordinate description of the complex in which each acetylene carbon atom is considered to occupy a separate coordination position is perhaps preferable to the alternative tetrahedral model where the alkyne occupies a single site (Fig. 2). The values of $\delta(C{\equiv}C)$ for $Mo(CO)(PhC{\equiv}CPh)_3$ are almost as low as those exhibited by Mo^{II} alkyne derivatives in which the alkynes can formally be considered as three-electron donors [13]. This is also in a very good agreement with King's [14] description of the bonding scheme applicable to $W(CO)(PhC{\equiv}CPh)_3$ complex in which a total alkyne donation of ten electrons formally corresponds to $3\frac{1}{3}$ electrons per unsaturated ligand.

Structural properties of the title compound are close to those for the tungsten analogue investigated earlier

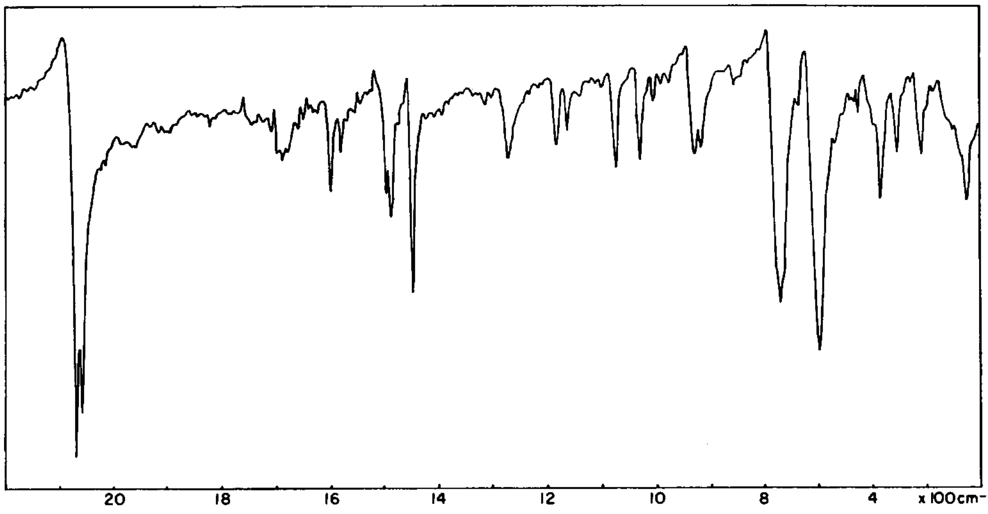

Fig. 3. IR spectra in the 2200–400 cm^{-1} region for $Mo(CO)(PhC{\equiv}CPh)_3$ in KBr pellets.

by Laine *et al.* [4] with a W–C_{ac} distance of 2.06 Å, a C_{ac}–C_{ac} distance of 1.30 Å, a C_{ac}–C_{ph} distance of 1.46 Å, a C_{ac}–W–C_{ac} angle of 36.4° and a W–C_{ac}–C_{ph} angle of 148.7°. The geometry of the coordinated diphenylacetylene molecules, interatomic distances and angles are very similar to those found in the monomeric molybdenum(II) alkyne complexes such as [$(C_5H_5)_2$Mo(PhC≡CPh)] and [MoTTP(PhC≡CPh)]$C_6H_5CH_3$ [15], but Mo(CO)(PhC≡CPh)$_3$ which we investigated is an unique example of an alkyne complex with molybdenum in the zero oxidation state.

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